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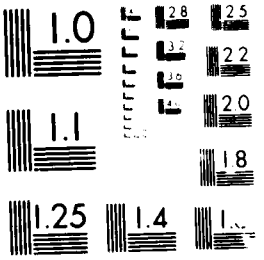
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TRANSPARENT GLASS CERAMICS DOPED BY CHROMIUM(III) AND CHROMIUM(III) AND NEODYMIUM(III) AS NEW MATERIALS FOR LASERS AND LUMINESCENT SOLAR CONCENTRATORS

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Introduction

Tunable lasers based on organic dyes are well known and their applications in various branches in physics and chemistry are well established by now. Because of degradation of the dyes under severe atmospheric conditions there is a need to replace the organic molecules by inorganic ions incorporated in a stable inorganic matrix which will have the optical properties and the tunability range of the organic dyes but will not suffer the disadvantage of degradation. One of such materials is single crystal alexandrite doped by trivalent chromium. During the first two years of the research we have shown that spectroscopic properties of Cr(III) in several singly doped glass-ceramics are comparable to those of alexandrite and the preparation is much easier and more economical. In our present research we are investigating the possibility of extending the tunability range and optimization of the performance of the glass-ceramics materials by co-doping with Nd(III).

The main goals of our research are:

1. To improve the microcrystallization of the glass-ceramics.
2. To increase the range of tunability.
3. To study energy transfer between Cr(III) and Nd(III) in glass-ceramics.
4. To calculate the threshold energies for oscillations of the tunable laser.

Having these goals in mind we prepared transparent glass ceramics doped with Cr(III) and Nd(III) from a precursor glass which forms mullite glass-ceramics [1]. In this environment the Cr(III) ions tend less to form aggregates than in other glass-ceramics [2] and the thermal equilibrium between the luminescent levels of Cr(III) assures wide emission range.

Experimental procedure.

The starting composition of the precursor glasses (in mole percent) was as follows; 45 SiO_2, 20 B_2O_3, 25 Al_2O_3, 10 K_2O, x Nd_2O_3, y Cr_2O_3 where the mole percents x and y are specified in Table I. The glasses were prepared by melting the precursor mixture in alumina crucibles in an electric furnace heated to

1600°C, then poured into a steel mould and placed in a furnace preheated to 650°C for annealing. The furnace was immediately turned off and the glases were cooled at the cooling rate of the furnace. For preparation of mullite glass - ceramics the glasses were heat treated in two steps; Samples containing 3 m.p. (an abbreviation for "mole percent") of Nd(III) were first heated to 700°C for 2 hours, then heated to 750°C for 3 hours and finally cooled at the cooling rate of the furnace; the samples containing 1 m.p. of Nd(III) were first heated to 750°C for 10 hours, then heated to 860°C for 2 hours and cooled at the cooling rate of the furnace. The material, when cooled down, was cut and polished. Mole percents of the dopants, thermal treatments and color of the glasses/glass-ceramics are summarized in Table I.

Table I: Preparation conditions of mullite glass-ceramics doped by Nd(III) and/or Cr(III).

# of sample	Nd(III) m.p.	Cr(III) m.p.	Thermal treatment T_1	Thermal treatment T_2	Color
1	1	0	-	-	pale lilac
2	3	0	-	-	lilac
3	1	0.1	-	-	green
4	3	0.1	-	-	lilac - green
5	1	0	750°C/10 hrs	860°C/2 hrs	very pale lilac
6	3	0	700°C/2 hrs	750°C/3 hrs	lilac
7	1	0.1	750°C/10 hrs	860°C/2 hrs	pale grey - lilac
8	3	0.1	700°C/2 hrs	750°C/3 hrs	greyish lilac
9	0	0.1	750°C/2 hrs	800°C/4 hrs	grey

Absorption spectra of the doped samples were measured on a Lambda-5 Perkin - Elmer double beam spectrophotometer against air since different sizes of the samples precluded the use of a single glass as a reference for all.
Emission and excitation spectra were measured on a home made spectrofluorimeter consisting of an Oriel 150 W Xenon lamp source, an Oriel excitation monochromator, a Spex-1704 analyzing monochromator and an Peltier cooled Hamamatsu 7102 photomultiplier coupled to a PAR-128 Lock-In Amplifier. All

measurements were performed at room temperature. It was not possible to compare the emission and excitation spectra obtained on the same intensity scale due to different geometries of the samples.

Lifetimes were measured using a tunable dye laser, Molectron-DL200 pumped by a Molectron UV-4 pulsed nitrogen laser at a repetition rate of 10 Hz and pulse duration of about 10 nsec. For excitation of chromium at 530 nm a Coumarin dye was used and for excitation of neodymium at 595 nm a Rhodamine 6G dye. The emitted light was passed through a monochromator and detected with a R928 Hamamatsu photomultiplier. THe signals were then sampled by a Biomation 8100 digitizer (10 nsec resolution) and averaged with a Nicolet 178 analyzer.
The averaged decay curves were then recorded on a YEW recorder. For further analysis the recorded signals were fed into a personal computer where they were processed.

Results and discussion.

Fig. 1 represents the absorption spectra of doped glass and glass-ceramics. Curve 1 represents the absorption spectrum of the precursor glass doped by 3 m.p. of Nd(III) and 0.1 m.p. of Cr(III). The absorption bands at about 650 nm and about 450 nm are due to low-field Cr(III) ions. Curve 2 represents the absorption spectrum of the precursor glass doped by 3 m.p. of Nd(III) without addition of Cr(III) and curve 3 represents the absorption spectrum of glass-ceramics doped by 3 m.p. Nd(III) and 0.1 m.p. Cr(III). The last shows very weak absorption bands due to Cr(III) in a high crystalline field [3]. The enhanced absorption at shorter wavelengths is due to Rayleigh scattering as confirmed by an analysis of polarization of the scattered light.

These absorption spectra serve as a basis for a complete set of predictions of transition rates within the $4f^3$ configuration of Nd(III). The procedure is based on the theory of Judd - Ofelt and is described in details elsewhere [4]. According to the theory the otherwise forbidden f - f transitions within the $4f^j$ configuration of a rare-earth ion become slightly allowed by admixing of wavefunctions of the configuration with odd components of the crystal field. The intraconfigurational transitions then become a subject to a new set of selection rules and oscillator strengths become dependent parametrically on three phenomenological parameters Ω_2, Ω_4 and Ω_6. The optical transitions of rare- earths in solids are mostly of electric dipole character and their intensities are given by formula,

$$S_{ed}(aJ:bJ') = e^2 \sum_t \Omega_t |\langle aJ||U^{(t)}||bJ'\rangle|^2 \qquad (1)$$

where t = 2,4,6 and the symbol in double brackets represents reduced matrix elements for the transitions. These are almost independent of surroundings and are tabulated for all rare-earth ions [5]. The values of the Ω's are calculated by solving an overdetermined set of linear equations in which the oscillator strenghts are the experimental values and the reduced matrix elements are taken from tables. Once found the three Ω's serve for calculation of all posssible transition rates for a particular ion in a particular surrounding, using the formula,

$$A(aJ:bJ') = \frac{64\pi^4\nu^3}{3hc^3(2J+1)} \left(\frac{n(n^2+2)^2}{9} S_{ed} + n^3 S_{md} \right) \qquad (2)$$

where S_{md} is the contribution of the magnetic dipole.

The parameters Ω_i for Nd(III) in the mullite glass-ceramics with and without Cr(III) are given in Table II and compared with the corresponding values in some other matrices.

Table II: Oscillator strength parameters for Nd(III) in mullite glass-ceramics and some other glasses.

glass	reference	Ω_2, [pm^2]	Ω_4, [pm^2]	Ω_6, [pm^2]
Silicate	[6]	4.0	3.3	2.5
Fluoride	[7]	1.0	3.7	6.2
Tellurite	[8]	4.7	5.1	6.1
Mullite	this work	2.4	1.9	2.8
Mullite +Cr	this work	2.3	2.0	3.2

Excitation spectra of glass-ceramics are shown in Fig.2. The spectra are vertically shifted for better visualization and are scaled to a similar height. Here curve 1 represents the excitation spectrum of glass-ceramics doped by 3 m.p. Nd(III) without Cr(III) and detected at 880 nm which corresponds to the transition $^4F_{3/2}$ --> $^4I_{9/2}$ of Nd(III). Curve 2 represents the excitation spectrum of mullite doped by 3 m.p. of Nd(III) and 0.1 m.p. of Cr(III) and detected at 695 nm, which corresponds to the transition from $^2E_2$ broadened by a

thermal equilibrium with the $^4T_2$ state to the ground state $^4A_2$ of Cr(III) ions in mullite [2]. The dip at about 580 nm observed in this spectrum is due to an absorption by the strong transition $^4I_{9/2} \longrightarrow {}^2G_{7/2}$ of Nd(III). In other respects this excitation spectrum is similar to the excitation spectrum of 0.1 Cr(III) in mullite glass-ceramics without Nd(III) [1]. Curve 3 represents the excitation spectrum of the same glass-ceramics but detected at 880 nm, the emission band of Nd(III). A substantial broadening and a change in the relative intensities of excitation bands are noted. These can be due to energy transfer from Cr(III) to Nd(III) but also to the contribution of the emission of Cr(III) at the detection wavelength.

Fig.3 represents emission spectra of Nd(III) and Cr(III) in mullite glass-ceramics excited at 550 nm and vertically shifted for better visualisation. Curve 1 represents the emission spectrum of mullite glass-ceramics doped by 0.1 m.p. of Cr(III). This is the characteristic emission band of the narrow $^2E_2$ line thermally equilibrated with the wide (and short lived) $^4T_2$ state and emitting together to the ground state, $^4A_2$. Curves 2 and 3 represent the emission spectra of mullite glass-ceramics doped by 0.1 m.p. of Cr(III) and co-doped by 1 m.p. and 3 m.p. of Nd(III) respectively. These curves are similar to curve 1 and dips at about 750 and 800 nm are due to the absorption by strong absorption bands of Nd(III) (compare with fig.1). The strong emission band at 820-920 nm is due to the transition $^4F_{3/2} \dashrightarrow {}^4I_{9/2}$ of Nd(III). Curve 4 represents the emission spectrum of 3 m.p. of Nd(III) in mullite glass-ceramics without Cr(III), excited at 550 nm. These spectra are not to-scale because of widely different geometries of the samples. Thus the emission (and consequently the tunability) range of the doubly doped glass-ceramics is wider than in glass-ceramics doped by Cr(III) only.

In addition to the radiative energy transfer observed in mullite doped by Cr(III) and Nd(III), the decrease of lifetime of Cr(III) in the presence of Nd(III) shows nonradiative energy transfer from Cr(III) to Nd(III). This effect is summarized in Table III. The samples were excited at 530 nm by a dye laser and the transient signals were detected at 695 nm, which is the wavelength of maximum emission of Cr(III) in mullite and at which Nd(III) does not emit. Due to high nonexponentiality of the decay curves we characterized the lifetimes by τ_1 and τ_2 where τ_1 is the time required for the transient signal to decay to the 1/e value of its intensity at time 0 and τ_2 is half of the time to decay to $1/e^2$ value of the initial intensity. In the case of an exponential decay these numbers are equal. The energy transfer yields, η_1 and η_2 are calculated from these numbers according to the formula:

$$\eta_i = 1 - \tau_i/\tau_o$$

where τ_o is the lifetime of Cr(III) in mullite without addition of Nd(III).

Table III: Lifetimes of Cr(III) in mullite co-doped by Nd(III).

# of sample	Nd(III) m.p.	Cr(III) m.p.	Lifetimes [μsec] τ_1	τ_2	Energy transfer yields η_1 [%]	η_2 [%]
3	1	0.1	60	136	71	35
4	3	0.1	19	52	91	72
9	0	0.1	208	600	0	0

Lifetimes of Nd(III) in these samples were found to be insensitive to the energy transfer process and vary between 220 and 260 μsec, similar to the lifetime of Nd(III) in mullite without Cr(III). This is expected since the energy transfer takes place on a short times scale and the amount of energy transferred (per ion of Nd(III)) is small due to the small absorption of Cr(III) in mullite glass-ceramics.

In the next stage of the investigation we will study spinel and gahnite glass-ceramics doped by Cr(III) and Nd(III) and will calculate the threshold energy for laser action in the doubly and singly doped glass-ceramics.

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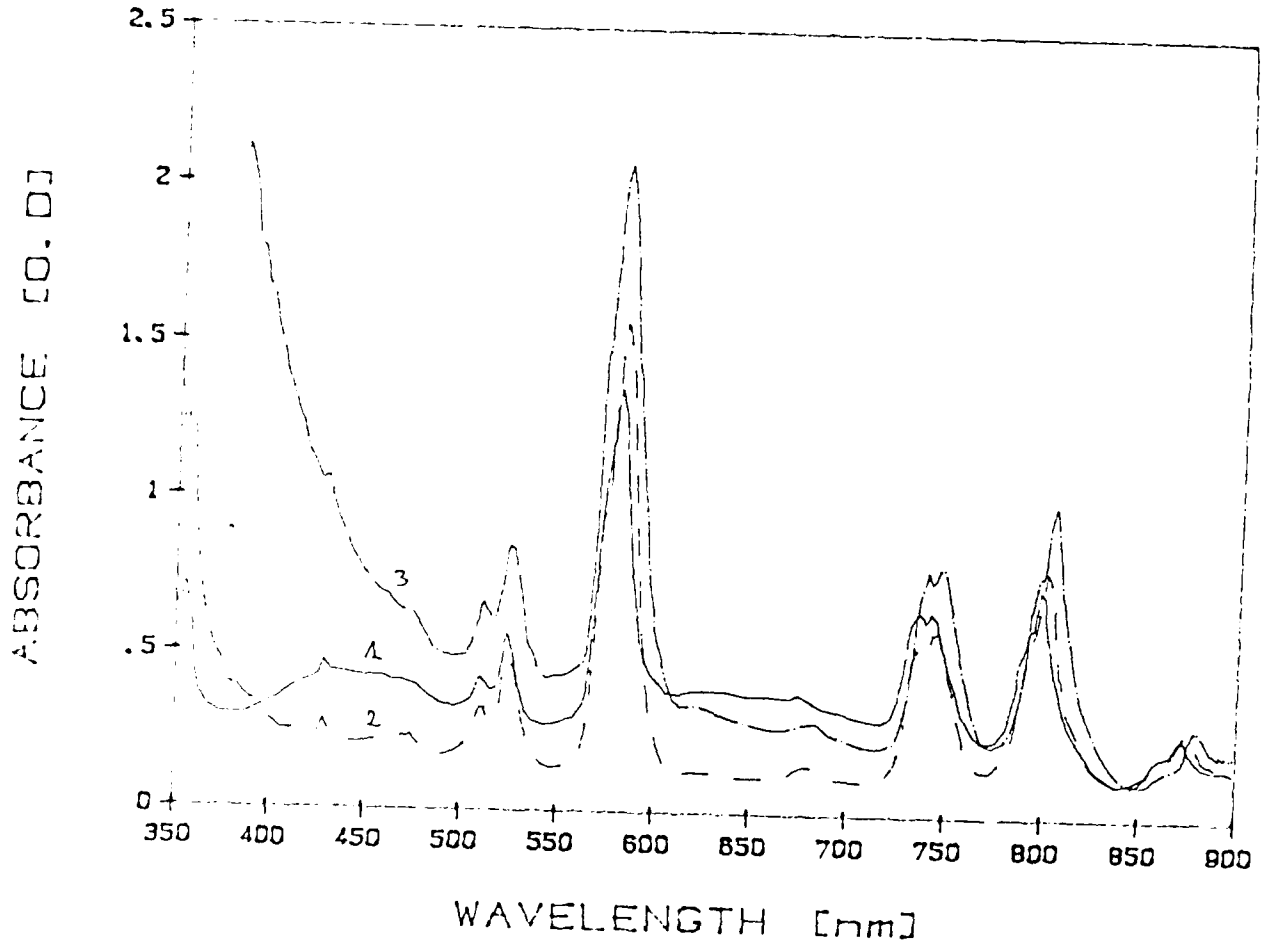
Figures captions.

Fig.1 :Absorption spectra:
Curve 1: 3 m.p. Nd(III), 0.1 m.p. Cr(III) in precursor glass. Curve 2: 3 m.p. Nd(III) in precursor glass. Curve 3: 3 m.p. Nd(III), 0.1 m.p. Cr(III) in mullite glass-ceramics.

Fig.2 : Excitation spectra.
Curve 1: 3 m.p. Nd(III) in mullite glass-ceramics, detected at 880 nm. Curve 2: 3 m.p. Nd(III), 0.1 m.p. Cr(III) in mullite glass-ceramics, detected at 695 nm. Curve 3: 3 m.p. Nd(III), 0.1 m.p. Cr(III) in glass-ceramics, detected at 880 nm.

Fig.3 : Emission spectra.
Curve 1: 0.1 m.p. Cr(III) in mullite glass-ceramics, excited at 550 nm. Curve 2: 1 m.p. Nd(III), 0.1 m.p. Cr(III) in mullite glass-ceramics, excited at 550 nm. Curve 3: 3 m.p. Nd(III), 0.1 m.p. Cr(III) in mullite glass-ceramics, excited at 550 nm. Curve 4: 3 m.p. Nd(III) in mullite glass-ceramics, exited at 550 nm.

Fig 1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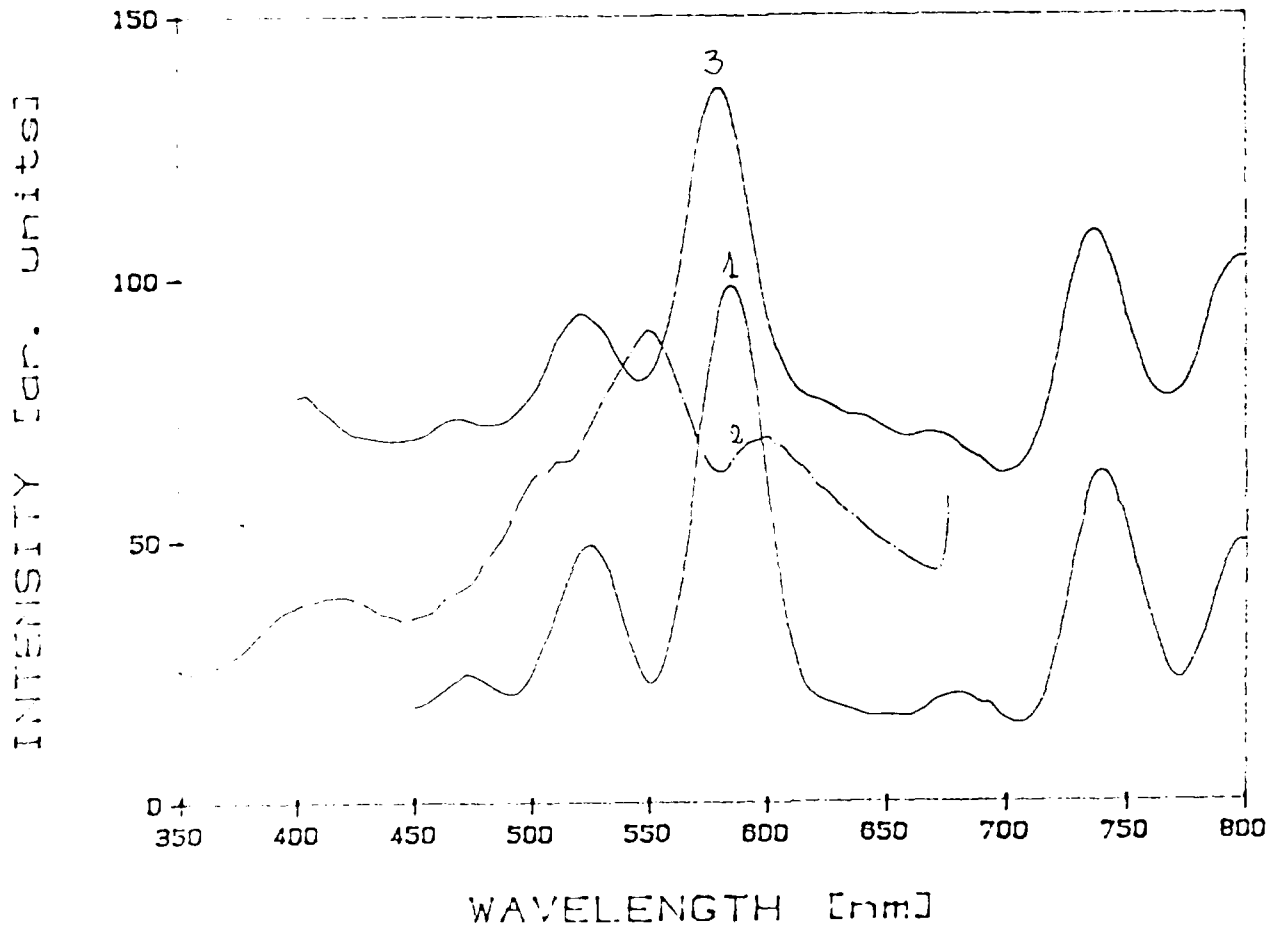
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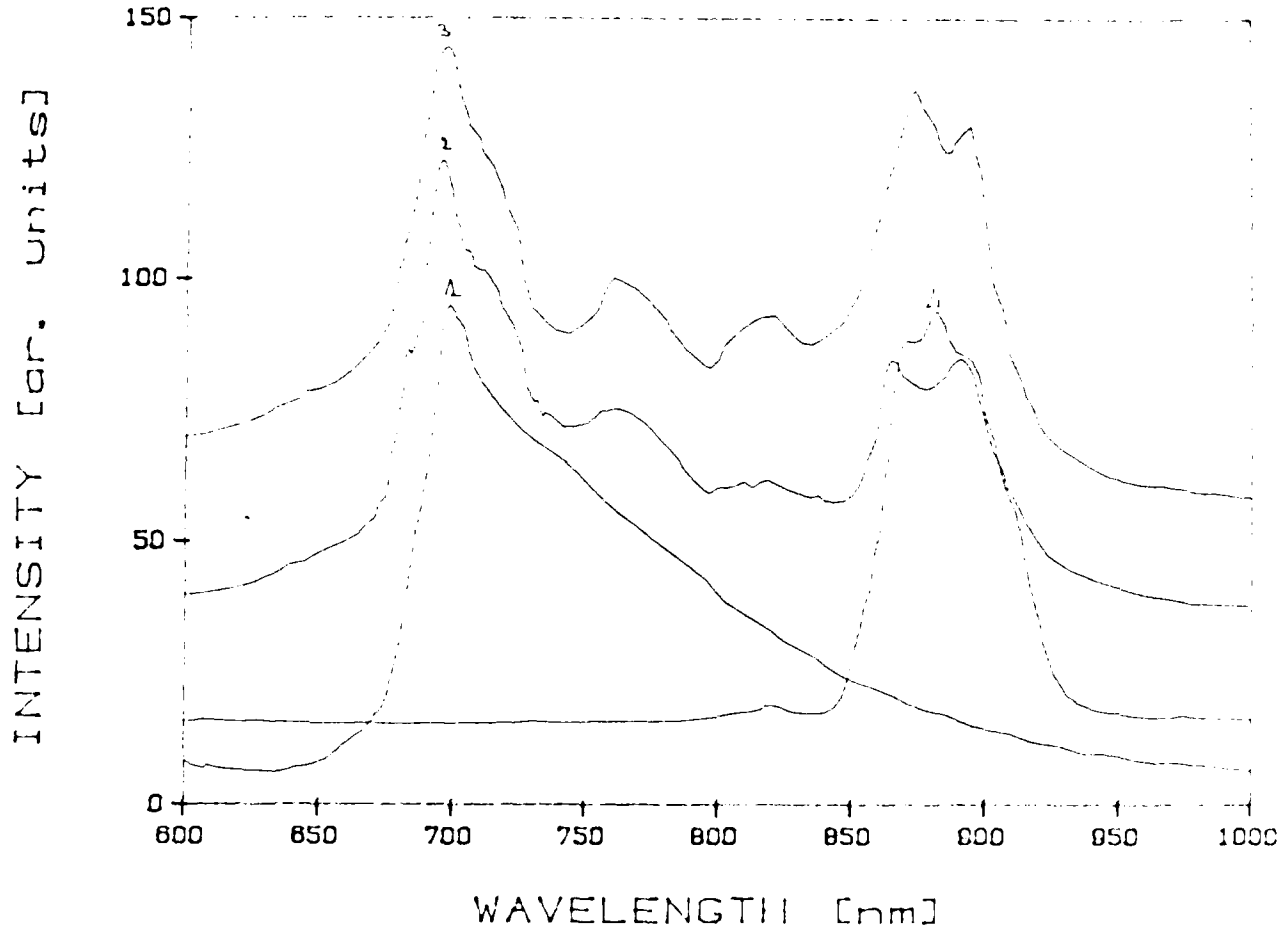
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